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Group 14 metallole dianions as η⁵-coordinating ligands

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As heavier aromatic analogs of the cyclopentadienides, group 14 dianionic metalloles exhibit more versatile reactivity and coordination modes due to the additional lone pair at the heteroatom. Compared to the well-established chemistry of monoanionic cyclopentadienide ligands, the coordination chemistry with those dianionic ligands remains underexplored. This perspective provides an overview of literature-known examples of group 14 metallole dianions (silole, germole, stannole and plumbole) adopting η⁵-coordinating modes. The diverse coordination modes and reactivity exhibited by these compounds highlight their potential as intriguing ligands in organometallic chemistry.

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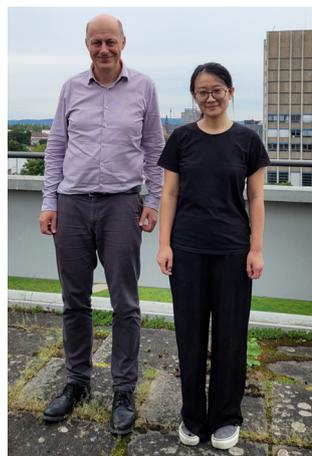
Xiaofei Sun (right) and Peter W. Roesky (left)

Xiaofei Sun obtained her BSc in 2016 and MSc in 2018 at Karlsruhe Institute of Technology (KIT). She joined the group of Professor Peter W. Roesky in 2018 to focus on group 14 chemistry and completed her doctoral degree in 2022. In 2023, she received the Südwestmetall Award for her doctoral thesis. Currently, she continues her work in the same group to further advance low-valent group 14 chemistry research.

Peter W. Roesky obtained his diploma in chemistry in 1992 from the University of Würzburg and his doctoral degree from the Technical University of Munich in 1994. After postdoctoral work at Northwestern University, USA (1995–1996), he completed his habilitation at the University of Karlsruhe in 1999. He was appointed a full professor at the Freie Universität Berlin in 2001, during which he joined the faculty of chemistry and biochemistry. In 2008, he became a full Professor of inorganic functional materials at the Karlsruhe Institute of Technology (KIT). From 2013 to 2015, he served as Dean of the Faculty of Chemistry and Biosciences at KIT. His current research interest revolves around the synthetic inorganic and organometallic chemistry of s-block metals, silicon, phosphorus, gold, and lanthanides.

1. Introduction

Dianionic group 14 metalloles (metallacyclopentadienediides) with the general formula of $[C_4R_4E]^{2-}$ (E = Si–Pb) are isolobal to the ubiquitous cyclopentadienide (Cp^-) monoanions (Fig. 1). Despite this close relationship, the coordination chemistry of such dianions has remained significantly underexplored. While the first generation of dialkalisiloles and -germoles was reported over 30 years ago,[1–4] recent advances of synthetic methods have facilitated further reactivity studies of those species.[5–8] Unlike the fully carbon-containing Cp^- adopting the conventional η⁵-coordination mode, heavy group 14 dianionic compounds exhibit more versatile reactivity and coordination modes due to the additional lone pair at the heteroatom. Quantum chemical calculations and experimental investigation reveal that the dianionic group 14 metalloles also exhibit aromatic character akin to the parent Cp^-.[9–12] The substitution of a ring C atom by a heteroatom result in a change in terms of the electronic properties. Moreover, the two negative charges on the metallole dianions facilitate the coordination of two metals in μ-η⁵:η⁵- or μ-η¹:η⁵-fashions, which is rarely achieved using monoanionic Cp^- derivatives. As a new generation of heterocyclic species, current research is primarily focusing on utilizing those metallole dianions as ligands in coordination chemistry and uncovering novel structures by
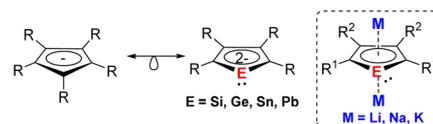

Fig. 1 Isolobal analogy between cyclopentadienide and dianionic metallole.

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X-ray diffraction analysis. Although additional applications, for example in catalysis and as single molecular magnets (SMMs), have recently emerged, the primary emphasis remains on structural discovery.

Several previous comprehensive review articles already exist dealing with the properties, synthesis and reactivity of those compounds.[9–12] This perspective specifically summarizes the literature-known examples of η^5-coordination modes of the metallole dianions.†

2.   Main group compounds

In 1990, Joo and co-workers for the first time reported the synthesis of the disodium salt of tetraphenylsilole by reduction of dichlorosilole with Na metal.[3] In the following decade, a handful of structurally authenticated germole and silole dianionic complexes have been reported. The X-ray structure of the lithium derivative [Li₂]1 (Fig. 2) was reported for the first time by West.[8] [Li₂]1 crystallizes as a monomer, with the two Li cations showing different coordination modes toward the silole ring (η^1 and η^5). Simultaneously, the tetramethylsilole dianion [K₂]2 (Fig. 2) was isolated and the X-ray structure was disclosed.[1,2] Compared to [Li₂]1, in [K₂]2 the two K cations are both coordinated by the silole ring in η^5-fashion and are complexed by 18-crown-6, which resulted in an inversed sandwich structure. Interestingly, in 1996, West obtained the X-ray structures for the dilithium salt of the tetraphenylgermole [Li₂]3a and [Li₂]3b (Fig. 2) from dioxane.[4] Depending on the crystallization temperature, the Li cations show distinct coordination modes ([Li₂]3a:η^5:η^5, [Li₂]3b:η^1:η^5) towards the germole ring. Also in 1996, in a comprehensive study about silole and germole compounds by Tilley, Rheingold and co-workers, the structure of the bis(germole) dianion complex [K₂]4 was

reported.[1] Later on the tetraethylgermole dianion [Li₂]5 was also structurally characterized.[13]

[Li₂]5 crystallizes as a one-dimensional coordination polymer with the germole ring being η^5-coordinated by two Li atoms and η^1-coordinated by one Li atom via the Ge lone pair. At that point, the scope of structurally characterized silole and germole dianions is only restricted to those possessing alkyl or aryl substituents.

In 2018, the Müller group reported the efficient multigram-synthetic protocol of the 2,5-trialkylsilyl-substituted dipotassium siloles [K₂]6 and [K₂]7 as well as germoles [K₂]8 and [K₂]9 (Fig. 2) from reduction of their corresponding neutral diha-lides.[5] The dipotassium salts [K₂]6–[K₂]9 possess very similar solid-state structures, all of them crystallize as one-dimensional coordination polymers, the silole rings are connected to each other with η^1- and η^5-coordinating potassium ions. This high-yield synthesis of the dianions has greatly advanced the chemistry to a new level and several fascinating novel compound classes could be approached by using [K₂]6–[K₂]9 as starting materials.[9] For instance, Albers and Müller obtained a neutral aluminocene 10 (Scheme 1) from the reaction of [K₂]8 with [Cp*AlCl₂] (Cp*⁻ = pentamethylcyclopentadienide).[14] Crystallographic studies demonstrated that it adopts a classical sandwich structure with the Al center positioned between the η^5-coordinating Cp* and germole ligands. Quantum chemical calculations showed that the Ge atom features an uncoordinated lone pair and a low-lying acceptor orbital, indicating its germylene character.

The dianions of the heaviest tin and lead analogs have remained elusive until the studies carried out by the Saito group. It was not until 2002 when the first synthesis of the dilithio-tetraphenylstannole [Li₂]11 (Fig. 3) was reported by reduction of the neutral bi(1,1-stannole) with lithium.[15] At that time, [Li₂]11 could not be isolated in pure form, but
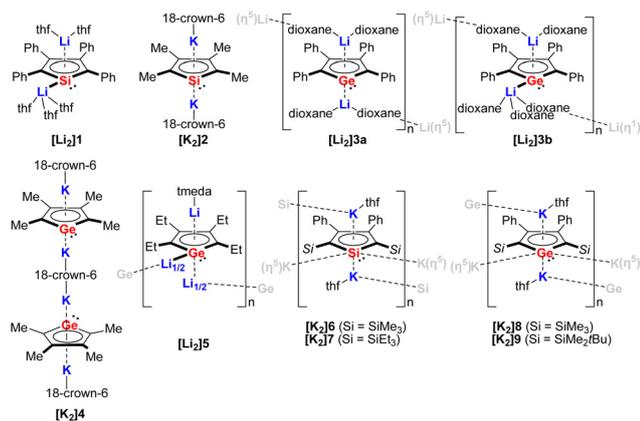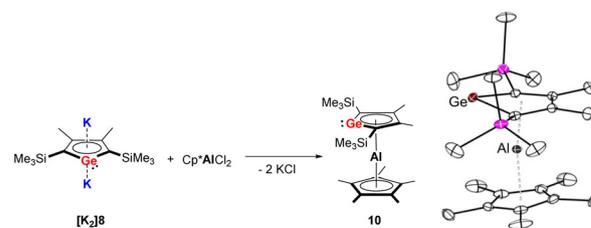

Fig. 2 Structurally characterized silole and germole dianion complexes.[1,2,4,5,8,13]

Scheme 1 Left: Synthesis of the germaaluminocene 10; right: molecular structure of 10 in the solid state with thermal ellipsoids at 40% probability. Reproduced from the CIF file having CCDC no. 1969078.[14]

**Fig. 3** Dilithiostannole and -plumboles from Saito.[6,7,15–18]

† Benzannulated dianionic metalloles will not be discussed in this perspective.

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trapped in the reaction with methyl iodide. In 2005, Saito succeeded in the isolation of $[Li_2]11$ as deep-red crystals in 98% yield.[16] The two Li cations are located above and below the stannole ring and each Li atom is coordinated to the stannole moiety in a η^5-mode and to one Et_2O molecule in η^1-fashion. The aromaticity of the stannole dianion was confirmed by X-ray diffraction analysis (bond lengths, planarity), NMR spectroscopy and nucleus independent chemical shift (NICS) calculations. Shortly after this initial report, the same research group published two additional reports describing the synthesis and structure of novel stannole dianions: the dilithiotetraethylstannole $[Li_2]12$,[17] and the dilithio-2,5-bis(silyl)-3,4-diphenylstannoles $[Li_2]13$ and $[Li_2]14$ (Fig. 3).[6] $[Li_2]12$ was isolated as black–yellow crystals in 57% yield that crystallizes as a one-dimensional coordination polymer, wherein one Li cation is coordinated by the stannole ring an η^5-fashion and one Et_2O molecule an η^1-fashion. The other Li cation displays η^5-coordination with one stannole and η^1-coordination with the Sn atom of another stannole, effectively linking the infinite polymer chain. The solid-state structures of the silyl-functionalized stannole dianions $[Li_2]13$ and $[Li_2]14$ bear resemblance to that of $[Li_2]11$, exhibiting inverse-sandwich structures with two Li cations being η^5-coordinated by the stannole unit and each of them coordinated by a THF molecule.

Five years after the isolation of the first stannole dianion,[16] Saito reported the synthesis and structure of the heaviest group 14 congener of the metallole dianions, namely, the dilithiotetraphenylplumbole $[Li_2]15$ (Fig. 3).[18] The synthesis of $[Li_2]15$ was accomplished analogously to that of the lighter analogs by reduction of the neutral metallole ring with elemental Li. Complex $[Li_2]15$ adopts a charge-separated structure upon crystallization from DME. In the anionic part, the Li atom is η^5-coordinated by the planar plumbole ring while the cationic part is composed of a DME-solvated Li atom. The authors further introduced bulky silyl groups in the 2,5-positions of the ring and synthesized another dilithioplumbole $[Li_2]16$ (Fig. 3)[7] which has a similar monomeric solid-state structure as the dilithiostannoles $[Li_2]11$, $[Li_2]13$ and $[Li_2]15$.

In recent work by Murugesu, the scope of the plumbole dianion 16^{2-} was expanded to its disodium and dipotassium salts, that are formed by reduction of the neutral plumbole with elemental Na or K (Scheme 2).[19] Depending on the solvent used for crystallization, the solid-state structures are
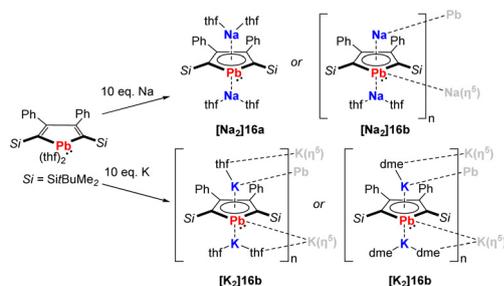
either monomeric ($[Na_2]16a$) or polymeric ($[Na_2]16b$, $[K_2]16a$, $[K_2]16b$). This breakthrough clearly showed that the stabilization of the dianionic plumbole ring does not necessarily rely on the η^5-coordination of lithium.

A very nice example illustrating the high reducing ability of the metallole dianions is the reduction of pentaphosphaferrocene and pentaarsaferrocene by the dilithioplumbole $[Li_2]16$ (Scheme 3).[20] As products, the heterometallic Fe–Li triple-decker compounds **17** and **18** were isolated, which are composed of Cp* and plumbole as end-decks and envelope-shaped $cyclo$-E_5 (E = P, As) units as middle decks. The plumbole rings maintained their planarity but the C–C bond lengths displayed alternating single and double bond character, therefore they are best described as plumbacyclopentadienylidenes.
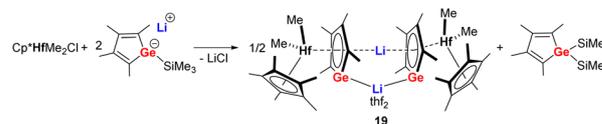
3. Transition metal compounds

Starting from the lithium salt of the germole monoanion, the first transition metal complex **19** (Scheme 4) comprising a germole dianion was prepared unexpectedly by reaction with $[Cp*HfMe_2Cl]$ *via* elimination of Me_3SiCl. The latter compound further reacts with one more equivalent of the germole monoanion to form the Hf(IV) germole complex **19** and bis(trimethylsilyl) germole as side product.[21] The Hf(IV) germole complex **19** crystallized as a dimer with one of the two Li cations being sandwiched between the two germole dianions in η^5-fashion while the other one is coordinated with both Ge atoms of the two germole rings.

Surprisingly, after this very initial report from the Tilley group in 2000, for a long time, no transition metal compounds with dianionic group 14 metallole ligand was reported, despite the fact that dialkalimetalloles should be ideal building blocks to construct double- or multi-decker complexes by simple salt metathesis reaction with suitable metal halide precursors.

This situation changed after Saito succeeded in the synthesis and isolation of the dilithium salts of stannole and plumbole. Using the dilithiostannoles $[Li_2]13$ and $[Li_2]14$
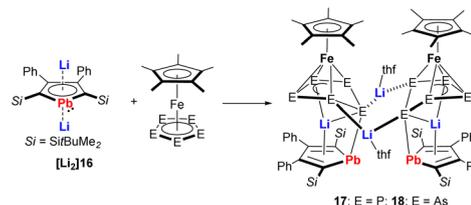
Scheme 3 Reaction of dilithioplumbole $[Li_2]16$ with pentaphospha- and pentaarsaferrocene.[20]

Scheme 4 Synthesis of the germole Hf(IV) complex **19**.[21]

Scheme 2 Synthesis of the disodium and dipotassium plumboles.[19]

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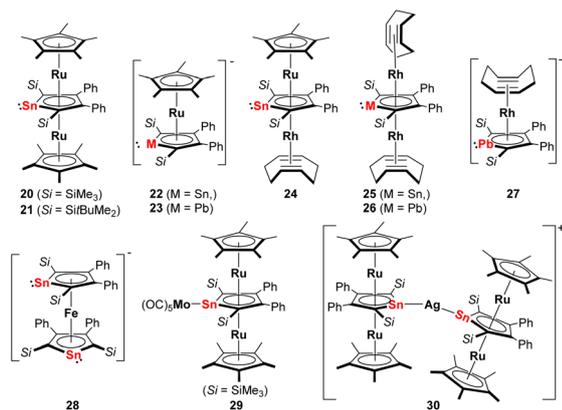*Inorg. Chem. Front.*, 2023, **10**, 5509–5516 | **5511**

Fig. 4 Late transition metal complexes with η^5-coordinating dianionic stannoles or plumboles; Si = SitBuMe$_2$, unless otherwise specified.[22–27]

bearing silyl and phenyl substituents, Saito and co-workers prepared the neutral triple-decker ruthenocenes **20** and **21** (Fig. 4) with Cp* ligands as end-decks and the middle stannole dianion coordinating the two Ru(II) metals in μ-η^5:η^5 mode.[22] This is a remarkable example since similar triple-decker species [(Cp-M)(μ-η^5:η^5-Cp)(M-Cp)]$^+$ (M = Fe, Ru, Ni)[28,29] composed of three Cp ligands are cationic and the introduction of such heterocycles with two negative charges enabled for the first time the isolation of a neutral analog. By changing the amount of [Cp*RuCl]$_4$, one Cp*Ru unit could also be incorporated to form the anionic stannole–Cp* double decker **22** (Fig. 4). More recently, the anionic ruthenocene **23** (Fig. 4) comprising the heaviest group 14 derivate, the plumbole dianion, was also reported.[23] NMR studies reveal that upon coordination of the plumbole to the Ru(II) center, the ^{207}Pb NMR signal appears at lower frequencies (1552 ppm) compared to that of **[Li$_2$]16** (2573 ppm). Calculations suggest that the difference is mainly attributed to the back-donation from Ru to the plumbole ring, which means an increase of electron density in the latter moiety is observed that leads to magnetic shielding on the nuclei in the plumbole ring.

Using the anionic ruthenocene **22** as precursor, the hetero-bimetallic Ru–Rh stannole triple-decker complex **24** (Fig. 4) could be accomplished.[25] By decomposition of **24** in ionic liquids [BMIm][BF$_4$] or [BMIm][NTf$_2$] (BMIm = 1-butyl-3-methyl-imidazolium; NTf$_2$ = bis(trifluoromethylsulfonyl) imide), the corresponding metal nanoparticles were prepared. The ionic liquids enabled the formation of non-agglomerated metal nanoparticle dispersion without the addition of capping ligands, polymers, or surfactants. For better comparison, the same group also synthesized the birhodium triple-decker species **25** (Fig. 4) by reacting **[Li$_2$]14** with [Rh(cod)Cl]$_2$ (cod = cyclooctadiene).[25] Analogously, the birhodium plumbole triple-decker complex **26** (Fig. 4) was prepared one year later.[27] In all these complexes, the stannole or plumbole rings coordinate the Ru(II) or Rh(I) atoms in an η^5-fashion. Due to the bulky substituents on the metallole rings, the two η^4-coordinating cod ligands in **25** and **26** are in a staggered arrange-

ment. When the amount of [Rh(cod)Cl]$_2$ in the reaction with **[Li$_2$]16** was reduced, the anionic Rh(I) complex **27** (Fig. 4) has also been achieved. Among those, the neutral plumbole complex **26** revealed high catalytic activity in the [2 + 2 + 2] cycloaddition of triynes, enabling the synthesis of benzene derivatives. Notably, the catalytic activity of the plumbole complex **26** surpasses that of [CpRh(cod)] which highlights the potential application of dianionic group 14 metalloles as an alternative to conventional Cp ligands in catalytic application.

Another intriguing example of applying metallole dianions in transition metal chemistry is the synthesis of the anionic stannaferrocene **28** which could be obtained from reaction of the respective dilithiostannole **[Li$_2$]13** with [Fe(acac)$_3$] (acac = acetylacetonate).[26] Complex **28** was isolated from a THF/ n-pentane mixture as dark purple crystals in 15% yield. The molecular structure (Fig. 5) clearly demonstrates that the central Fe ion is sandwiched between the two planar η^5-stannole rings, therefore exhibiting great structural resemblance to the archetypical sandwich compound ferrocene. To minimize steric hindrance, the two nearly identical stannole moieties adopt *gauche* conformation. Due to the strong reducing nature of the dilithiostannole, the formal oxidation state of the iron center should be +1, as evidenced by Mössbauer spectroscopy and quantum chemical calculations, resulting in formally mono anionic ligands.

More recently, the Saito group employed the triple-decker ruthenocene compounds **20** and **21** as novel stannylene ligands for other transition metals.[24] The reaction of **20** with [Mo(CO)$_6$] furnished the triple-decker Mo(CO)$_5$ complex **29** (Fig. 4) in which the stannole lone pair coordinates the Mo(0) moiety. Upon complexation, the geometric parameters of the triple-decker fragment remain almost unchanged. Alternatively, the Ag complex **30** that is linearly coordinated by two triple-decker units, could also be synthesized by reacting two equivalents of **21** (Fig. 5) with a Ag(I) carborane. The two triple-decker motifs in **30** are oriented perpendicularly to each other due to steric congestion arising from the bulky silyl substituents. This efficiently showcased that multi-decker metallole complexes can act as strongly electron-donating tetrylene ligands by coordinating the lone pair toward a second metal fragment in η^1-fashion.
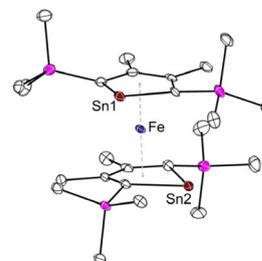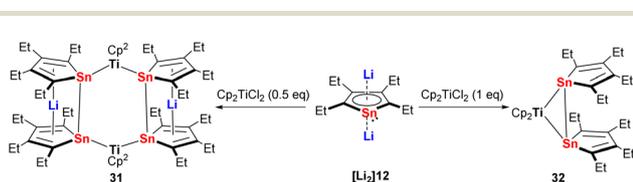

Fig. 5 Molecular structure of the anion of Saito's stannaferrocene **28** in the solid state with thermal ellipsoids at 40% probability. Reproduced from the CIF file having CCDC No. 1859348.[26]

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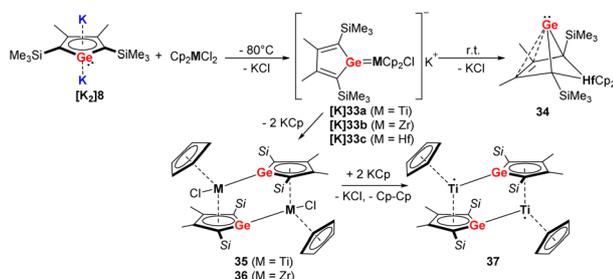This journal is © the Partner Organisations 2023

The reactivity of the metallole dianions is influenced not solely by the heteroatom but also by the ring substituents and the solvent used in the reaction. As discussed before, sandwich-type Ru(II) stannole complexes **20**, **21** and **22** were obtained when the silyl-functionalized stannole dianion was employed. However, using the tetraethyl stannole dianion and the same Ru(II) starting material [Cp*RuCl]$_4$, dinuclear Ru(II) species with butterfly of inverse-sandwich structures were isolated.[30] During the investigation of the reactivity of the dilithiostannoles with the early transition metal precursor [Cp$_2$HfCl$_2$], it turned out that the outcome of the reaction depends on the solvent which was used.[31,32] For instance, when the bulky silyl-functionalized dilithiostannole [Li$_2$]**14** was employed, the salt elimination reaction in toluene led to the formation of a dinuclear Hf(IV) complex in which the two Hf(IV) fragments are both coordinated by the stannole in η^1-fashion.[32] In sharp contrast, the same reaction in THF resulted in the formation of a pyramid-like Hf(IV) complex.[31] The analogous reaction of the tetraethylstannole dianion [Li$_2$]**12** with [Cp$_2$TiCl$_2$] gave the six-membered Sn$_4$Ti$_2$ ring complex **31** or the three-membered Sn$_2$Ti ring complex **32** depending on the molar ratio of the two starting materials (Scheme 5).[33] During the reaction some redox processes were taking place leading additionally to unidentified low-valent Ti(III) compounds. **31** can be regarded as the reduced version of **32** and was alternatively obtained quantitatively by the reduction of **32** with dilithiostannole [Li$_2$]**12**. In complex **31**, the two lithocene moieties are connected with each other *via* the two bridging Cp$_2$Ti fragments.

When the germole dianion [K$_2$]**8** was reacted in a similar procedure with group 4 metallocene dichlorides [Cp$_2$MCl$_2$] (M = Ti, Zr, Hf) (Scheme 6), the outcome of the reaction is different compared to the heavier Sn analog.[34–36] In the case of

Hf, the bicyclic germylene **34** was formed *via* anionic hafnocene germylene intermediate [**K**]**33c**.[36] For the lighter metals Ti and Zr, the dimeric Zr(IV) germole complex **36** or Ti(III) complex **37** were isolated (Scheme 6).[35] The formation of the latter compound proceeds *via* the intermediate **35**, which was isolated in small amounts. When the Hf compounds [**K**]**33c** or **34** were further used in the reactions with the tetramethylimidazolylidene or [PPh$_3$AuCl], the ligand underwent rearrangement.[34]

4. Rare-earth compounds

The reactivity of dianionic metalloles has already been investigated to some extent, particularly in relation to transition metals. However, in comparison, rare-earth complexes comprising group 14 metallole dianions are extremely scarce. Progress has been made in this area since 2021 when Tan and co-workers expanded the coordination chemistry of the metallole dianions to rare-earth elements and isolated a series of yttrium germole complexes **38–40** (Fig. 6).[37] The reaction between the dipotassium germole [K$_2$]**8** with YCl$_3$ in equimolar ratio in THF did not lead to the conventional salt elimination product. Instead, the dianionic yttrium germole salt [(η^5–**8**)YCl$_3$][K(2.2.2-crypt)]$_2$ (**38**) was isolated as yellow crystals after the addition of 2.2.2-cryptand to the reaction mixture. The Y(III) atom in **38** is coordinated by the germole dianion in an η^5-fashion with a Y–Ct$_{Germole}$ distance of 2.331 Å. When the molecular ratio between [K$_2$]**8** and [YCl$_3$(thf)$_{3.5}$] was changed to 2 : 1 and the reaction was performed in toluene at 80 °C, the salt metathesis proceeded and complex **39** could be isolated as dark brown crystals in 24% yield. Complex **39** crystallizes as a

Scheme 5 Reaction of tetraethyldilithiostannole [Li$_2$]**12** with [Cp$_2$TiCl$_2$], leading to the formation of **31** and **32**.[33]

Scheme 6 Reaction of Müller's dipotassiogermole [K$_2$]**8** towards group 4 metallocene dichlorides.[35,36]
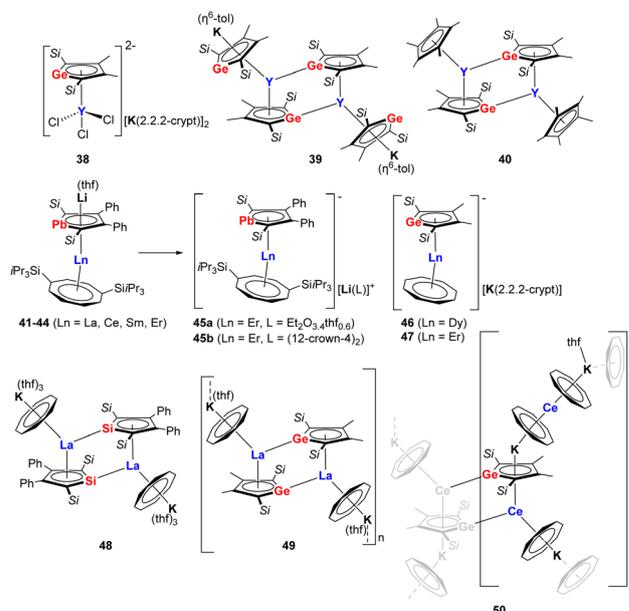
Fig. 6 Rare-earth compounds with η^5-coordinating metallole dianions.[37–40]

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dimer with each Y center being η^5-coordinated to two *trans*-oriented germole dianions. In addition, each Y(III) atom exhibits an additional η^1-coordination with the neighboring germole ring. Moreover, the two K atoms are coordinated in an η^5-fashion to the germole ring and in an η^6-fashion to a toluene molecule. A similar dimeric dinuclear Y species **40** was obtained by the reaction of $[\mathbf{K_2}]\mathbf{8}$ with $[Cp^*YCl_2]$, the two yttrium centers are both coordinated by one germole moiety and one Cp^* moiety in η^5-interaction modes.

It is interesting to note that the Roesky group achieved the isolation of a series of monomeric lanthanide sandwich compounds comprising the heaviest 14 metallole dianion (**41–45b**, Fig. 6) upon treating the dilithioplumbole $[\mathbf{Li_2}]\mathbf{16}$ with suitable lanthanide borohydride precursors $[Ln(\eta^8\text{-}COT^{TIPS})BH_4]$ (COT^{TIPS} = 1,4-bis-triisopropylsilyl-cyclooctatetraendiide).[38] Four isostructural sandwich species **41–44** (Ln = La, Ce, Sm, Er) were obtained through crystallization from *n*-heptane (**41**, **42**, **44**) or toluene (**43**), among which the erbium congener **44** exhibits magnetic hysteresis up to 5 K, providing unequivocal evidence of single molecule magnet behavior. Interestingly, the Li cation could be trapped by crystallization from Et_2O (**45a**) or addition of 12-crown-4 (**45b**), which has led to modulation of the magnetic properties of the Er complex due to slight changes in the bonding metrics of the central $[(\eta^5\text{-}\mathbf{16})Er(\eta^8\text{-}COT^{TIPS})]^-$ fragment.

Another noteworthy example of near-linear (*approx.* 175°) lanthanide group 14 metallole sandwich complexes (**46–47**, Fig. 6) was described by the Layfield group in 2023.[39] In this case, the germole-ligated $[K(2.2.2\text{-crypt})][(\eta^5\text{-}\mathbf{8})Dy(\eta^8\text{-}COT)]$ (**46**) and $[K(2.2.2\text{-crypt})][(\eta^5\text{-}\mathbf{8})Er(\eta^8\text{-}COT)]$ (**47**) complexes were synthesized by reacting $[\mathbf{K_2}]\mathbf{8}$ with $[(\eta^8\text{-}COT)Ln(BH_4)(thf)_2]$ in 1 : 1 THF and toluene mixture. The $Ln\text{-}Ct_{Germole}$ distances are 2.3063(2) (**46**) and 2.2693(10) Å (**47**). Remarkably, the axial geometry provided by germole is maintained as the lone pair of Ge do not engage in bonding interactions with nearby Ln(III) ions. Based on magnetic measurements, the Dy(III) complex (**46**) did not feature SMM behavior, while for the Er(III) analog (**47**) a magnetic hysteresis loop up to 10 K was observed.

Roesky *et al.* also highlighted that different combinations of the dianionic silole $[\mathbf{K_2}]\mathbf{6}$/germole $[\mathbf{K_2}]\mathbf{8}$ and early Ln(III) ions (La, Ce) in combination with the cyclooctatetraendiide ligand can lead to different dimensionality and intermolecular interactions.[40] These includes a dimeric La–silole complex (**48**, Fig. 6), a La(III)–germole ladder-type 2D polymer (**49**) and a Ce(III)–germole 3D coordination polymer (**50**).

5. Conclusion and perspectives

The coordination chemistry of group 14 metallole dianions has already yielded significant findings in both in p- and d-block chemistry and recently this chemistry was extended to f-block metals. This expansion of the field highlights the versatility and potential of metallole dianions in diverse areas of chemistry. To cater to more specific applications, the incorporation of ring heteroatoms offers electronic fine-tuning capabilities that cannot be achieved with solely carbon-based ring systems. In particular, the synthesis of dianionic group 14 metalloles has become more straightforward and advanced, which plays pivotal role in their further application and investigation. Despite the significant progress made in this area in the past twenty years, the periodic table of elements still offers abundant opportunities for future investigations of the reactivity of group 14 metalolle dianions. There remains significant untapped potential for utilizing such intriguing heterocycles as ligands to stabilize novel structure motifs. The combination of metallole dianions with diverse metal centers opens up great possibilities for discovering new catalytic processes, designing advanced luminescent materials, and developing high-performance magnetic compounds. Thus, it was already shown that the heteroatoms have an influence on the SMM properties of the corresponding lanthanide complexes and that the magnetic properties can be modulated. Present investigations of the catalytic properties are mainly limited to Rh(I) complexes. However, since the classical Cp complexes of various d- and f-elements have a wide range of catalytic applications depending on the metal used, it can be assumed that the potential of group 14 metallol complexes in catalysis is far from being fully explored. As research in this area continues to progress, we anticipate that in the near future investigations will give more exciting results.

Author contributions

X. S. – investigation and writing. P. W. R. – writing, reviewing and editing.

Conflicts of interest

There are no conflicts to declare.

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